Whether in catalysis, biology or the protection of the environment, fluorinated functional materials are emerging as important chemical tools to achieve improved performance and higher stability under a variety of conditions. Providing a distinct increase in molecular hydrophobicity, fluorination allows easy tuning of a material’s hydrophilic–lipophilic balance (HLB), in particular with sol–gel materials obtained by polycondensation of fluorinated precursors. Reporting on recent remarkable achievements, this review attempts to show the large unexplored potential of these materials.

1. Introduction

New functional fluorinated materials are rapidly emerging to meet the demanding requirements of advanced applications in fields as diverse as sensing, catalysis and environmental protection. Indeed, in the last five years modern materials science, quantum chemistry and biochemistry have opened the way to the synthesis of new fluorinated materials possessing extraordinary properties such as crosslinkable dendrimers for the fabrication of optical waveguides of low optical loss and excellent thermal stability; highly effective and recyclable absorbents for oil and heavy metals; gelling polymers with excellent optical and electrical properties; highly sensitive oxygen optical sensors; materials for in vivo oxygen transport (potential blood substitutes), diagnosis and drug delivery; liquid-crystals for high-performance displays; self-assembling polymeric supramolecules; high-performance catalysts for aerobic conversions in CO$_2$; single-wall carbon nanotubes; photoresists for the next generation of chips; and thermoplastic polymers showing elastomeric behavior between −75 °C and 100 °C.

Not surprisingly, a vast number of novel findings in functional fluorinated materials (Table 1) are being reported by the leading international scientific journals, while so called “fluorous phase” synthetic methods have evolved into mainstream chemistry practices with major suppliers of laboratory chemicals now offering fluorinated reactants and materials.

Books and review articles on fluorine chemistry and its applications are being published on a regular basis. Therefore, the main objective of this work is to report the emerging new applications and to outline the general potential of these materials.
concepts, and available methodologies, through which chemists and materials scientists using an ingenious integrated approach will be able to tailor the properties of new functional fluorinated materials for targeting specific applications. This review ends with some brief considerations of the environmental and economic aspects of fluorinated materials.

2. Principles and methodologies

Fluorine atoms bind tightly to carbon in organic molecules and modest fluorination of the molecular structure leads to large changes in the physical and chemical properties of that molecule, imparting to fluoro-organic compounds with a variety of new functional properties, including: (i) enhanced hydrophobicity (but, high lipophobicity in perfluorinated substances), (ii) high thermal and oxidative stability (resistance to sunlight), (iii) weak intermolecular interactions, and (iv) low surface energy and surface tension. Moreover, fluorinated substances generally show: (v) a low refractive index (low light absorption), (vi) exceptional chemical and biological inertness, (vii) high gas-dissolving capacity, and (viii) high fluidity and density (for liquids).

Several fluorinating agents exist and new nucleophilic and electrophilic fluorination reactants are regularly being discovered. Here we will briefly mention pure anhydrous tetrabutylammonium fluoride (TBAF), whose novel synthesis provides chemists with a “naked” fluoride ion acting as a nucleophile with a reactivity that is comparable to, or exceeds, that of other nucleophilic fluorinating reagents and “select-fluor” [1-chloromethyl-4-fluoro-1, 4-diazoniabicyclo[2.2.2]-octane bis-(tetrafluoroborate)], a highly reactive, non-toxic, and easy to handle electrophilic fluorinating reagent that is replacing dangerous and less selective F2 in the industrial synthesis of a variety of pharmaceutical and agricultural products. For example, prediction of the absorption spectra of fluorinated molecules and polymers can be used to identify the minimum number of fluorine atoms that are necessary to generate a fluorous phase. Quantum mechanics and ever growing computational power allow the prediction of the electronic properties of an increasing number of molecules and materials; for example, prediction of the absorption spectra of fluorinated monomers leads to the preparation of molecules which impart the desired properties to the fluorinated material.

Due to the anomalous physico-chemical properties of fluorinated organics, it is no surprise that fluorine incorporation into biologically active compounds, altering drug metabolism and enzyme substrate recognition, has a number of relevant consequences in life sciences. Moreover, biochemical research recently resulted in the discovery of the first fluorinase enzyme that has the capacity to catalyze the formation of a carbon–fluorine bond: a fundamental discovery offering a new opportunity for the preparation of organofluorine compounds as, once the gene coding for the fluorinase has been identified it will be copied and inserted into other organisms to generate novel fluorine-containing compounds by fermentation.

The most abundant halogen element, fluorine is the most electronegative element and one of the least polarizable atoms in the periodic table. After hydrogen and helium, the fluorine atom has the smallest atomic radius (0.64 Å). The C–F chemical bond is the strongest known single bond in organic chemistry (ca. 450 kJ mol⁻¹) and hydrogen atoms in hydrocarbons can be replaced with fluorine atoms to practically any extent from mono- to perfluoro-substitutions. Fluoropolymers, in addition to the known advantages offered by other elastomers (thermoelastic behaviour, easy fibre and coating production, traction resistance etc.), show pronounced hydrophobicity and high physical and chemical stability that make them suitable materials for a number of uses requiring these properties. For example, the corrosion resistance of gaseous UF₆ was employed in the Manhattan Project to extract the uranium isotope needed for nuclear fission; PTFE found immediate application despite its high cost and later became widely employed for coating bakeware and, in the textile industry, to make transpiring fabric from expanded porous PTFE membranes.
characterization techniques endeavouring to explain the dielectric constant reduction.27

\[
\text{SiO}_3\text{OH} + \text{HF} \rightarrow \text{SiO}_3\text{F} + \text{H}_2\text{O}
\] (1)

The electrical and thermomechanical properties of SiO₂, in fact, are ideally suited as interlayer dielectrics in microelectronics but materials with lower dielectric constants \(k\) are needed for advanced interconnect applications. Fluorinated silica glass, having a dielectric constant lower than that of F-free \(\text{SiO}_2\), is among the best low-\(k\) candidate materials (Table 2).28

Calculations suggest that it is the ionic component of the dielectric constant that is mostly affected by the F incorporation. Furthermore, molecular orbital calculations conducted for various cluster models of silica and for those of fluorinated silica indicate that the heat of formation of FSG per Si tetrahedral unit decreases with an increasing number of Si tetrahedral units (which, in its turn, depends on the preparation conditions). Remarkably, the addition of HF to silica clusters gave a F–Si bond in trigonal bipyramid geometry for a five-coordinated Si.29

As a further example, the molecular basis of CO₂ interaction with fluorinated polymers has been investigated by computational chemistry on model compounds and molecular simulation of polymers such as poly(trifluoropropyl methyl siloxane) and poly[bis(2,2,2-trifluoroethoxy)phosphazene] that exhibit high CO₂ permeability and preferential permeation.30

The results indicate that CO₂ forms a favorable quadrupole–dipole interaction (Fig. 1) with the fluoroalkyl groups whose maximum interaction energy (–11.5 kJ mol⁻¹) for \(\text{CO}_2\)-CF₃CH₂CH₃ is less than typical interaction energies for hydrogen bonding, but greater than the London dispersion values for the interaction of CO₂ with a carbonyl group.

Electrostatic potential distributions indicate a small redistribution of electron density to the fluorine atoms of the trifluoroalkanes and to the oxygen atoms of CO₂ in the \(\text{CO}_2\)-CF₃CH₃ and \(\text{CO}_2\)-CF₃CH₂CH₃ dimers. In addition, pair-correlation analysis by molecular dynamics simulation shows a strong correlation of CO₂ with the trifluoromethyl group of PTFEP in agreement with the \(\text{ab initio}\) molecular orbital calculations which show an association of CO₂ with both CH₃CF₃ and CH₃CH₂CF₃. Again, these computational results not only give an explanation of the solubility of many fluorinated polymers in dense phase carbon dioxide, but suggest, for instance, that since close physical association (less than 4.3 Å between the centres of mass) between CO₂ and fluorinated groups is necessary to ensure optimal solubility, fluoropolymers with bulky groups, such as 6-F polyimides (polyimides derived from 4,4’-hexafluoroisopropylidene-dipthalic anhydride), will be considerably less soluble in this environmentally benign solvent.

Fig. 1 Fluorinated polymers exhibit high CO₂ solubility. Calculations indicate a favorable interaction between CO₂ and the polar fluorocarbon moieties and suggest that quadrupole-dipole interaction (the interaction of CO₂ with the trifluoroethane moiety is shown here) is an important contribution to the total energy of interaction.30

![Diagram](Image)

**Table 2** A list of low-\(k\) candidate materials for novel dielectrics in microelectronics

<table>
<thead>
<tr>
<th>Material</th>
<th>(k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorinated silica</td>
<td>3.2–3.6</td>
</tr>
<tr>
<td>Polyimides</td>
<td>3–3.5</td>
</tr>
<tr>
<td>Hydrogen silsequioxane</td>
<td>2.8–3.0</td>
</tr>
<tr>
<td>Methylated silica from MTMS</td>
<td>2.7</td>
</tr>
<tr>
<td>Fluorinated polyimides</td>
<td>2.5–3.0</td>
</tr>
<tr>
<td>PTFE (teflon)</td>
<td>1.9</td>
</tr>
<tr>
<td>Fluorinated carbon</td>
<td>2.1–2.5</td>
</tr>
</tbody>
</table>

* Measured in the out-of-plane direction at \(v = 1\) MHz

In materials science, sol–gel science and technology have made it possible to merge the (huge) domains of organic and ceramic chemistry, allowing the preparation of highly reactive porous oxides, including fluorinated materials, doped with practically any organic molecule and, at the same time, precise control of an immense range of structural properties of the resulting materials.32

Organic compounds rarely survive temperatures above 200 °C, while inorganic polymers (ceramics) are usually formed at temperatures >1000 °C. The mild, liquid-phase polycondensation of metal alkoxides typical of the sol-gel process has therefore opened the route to a vast class of extremely reactive glassy materials (doped oxides called xerogels or aerogels, depending on the drying method used to deissecte the intermediate alcogel, Scheme 1). Sol–gels have found applications in fields as diverse as optics, sensing, catalysis, electrochemistry and photochemistry due to their...
3. Applications

In the following, a selection of novel applications of fluorinated materials is reviewed in order to show the impressive versatility of these materials and how, in practice, the concepts highlighted above are being applied by chemists and materials scientists.

3.1 Hydrophobic surfaces

Hydrophobic fluorinated surfaces have a number of useful applications. In nature, a hydrophobic effect is observed on the leaves of the lotus plant due to the microscopic roughness of the leaf surface decorated with hydrophobic wax; this hydrophobic behaviour can be mimicked by ultrahydrophobic fluorinated nanocomposite films (i.e. surfaces exhibiting large water-contact angles) (Fig. 2).

In one approach, fluorinated polyanions and polycations are used to coat the particles of the mineral attapulgite with a hydrophobic layer, forming clusters which produce micrometre scale roughness. Hence, a sequential layer-by-layer tri-strata assembly approach is used to produce the ultrahydrophobic surfaces: the first stratum consists of several layers of pairs of poly(diallyldimethylammonium) cations [PDADMA] and poly(4-styrenesulfonate) anions deposited from a salt solution onto a silicon wafer; the second stratum consists of alternating layers of clay particles bearing a negative surface charge and PDADM and the final stratum is made of layers of two fluorinated polyelectrolytes.

Using a similar approach, the tidy topography of the lotus leaf is mimicked using a simple, water-based process, in which micrometre-sized pores are first created on a polyelectrolyte multilayer surface (by adding acid), and then silica nanoparticles are deposited onto the material, followed by a semifluorinated silane coating. The material retains its superhydrophobic character even after being immersed in water for a week, while elimination of the semifluorinated silane coating step, makes the material super-hydrophilic.

Suitable for use as optical waveguides due to their low refractive index and energy absorption along with excellent UV-imprinting properties.

High sensitivity to external reactants, transparency and enhanced chemical and physical stability.

In the case of fluorinated substances, fluorine being easily bound to carbon in hydrolytically-stable metal alkoxides, a wide variety of fluorinated alkoxide precursors are easily synthesised which can be used for the synthesis of hybrids with several potential applications.

Fluorinated ORMOSIL (organically modified silicates), in particular, are finding a number of remarkable applications due to the extraordinary properties imparted by fluorine to these organic–inorganic nanocomposites. In general, in fact, fluorination of the inorganic matrix largely enhances its thermal and chemical stability as well as the surface properties of fluorocarbon hybrid gels resulting in higher hydrophobicity and oleophobicity than in hydrocarbon ORMOSIL homologue gels.

In particular, best results in terms of thermal stability and hydrophobicity are observed for materials produced by sol-gel hydrolysis of fluorooalkyl mono-functional trimethoxysilanes such as that represented in eqn (2) with the fluorocarbon moieties ending segregated at the surface of the material’s cages

$$\text{CF}_3(\text{CH}_2)_3\text{Si(OCH}_3)_3 + \text{H}_2\text{O} \rightarrow \text{[CF}_3(\text{CH}_2)_3\text{SiO}_n\text{H}_{2n-1} + \text{CH}_3\text{OH}}$$

This directly affects the reactivity and sensitivity of the final doped ORMOSIL materials because in the case of doped sol–gels, the reaction takes place at the cage’s surface where the entrapped dopant molecules are accessible to external reactants. Finally, the optical properties of highly fluorinated and photosensitive ORMOSIL-derived films make them suitable for use as optical waveguides due to their low refractive index and energy absorption along with excellent UV-imprinting properties.

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Having a low coefficient of friction and being inert like many fluorinated surfaces, these materials are potentially useful for the development of materials with bioadhesive (or bioinert) surfaces, thus favouring (or preventing) protein adhesion depending on the surface charge and on the tuneable HLB of the polyelectrolyte multilayers. Indeed, cells cultured on the hydrophobic surface of a positive fluorinated polyelectrolyte spread and adhere, whereas cells cultured on a hydrophilic surface of multilayers of a zwitterionic copolymer do not adhere.  

Another example of the enhanced sorption properties of fluorinated materials is provided by self-cleaning coloured materials obtained by simple treatment with a fluoroalkylsilane of a mesoporous silica gel in which striking colors, like those of butterfly wings, come from light diffracting off the ordered silica nanostructure and hydrophobicity benefits the material by shedding water and dirt.  

3.2 Separation and environmental protection

Fluorous solid-phase extraction is used for quick separations of reaction mixtures involving fluorous reagents, protecting groups, tags, and scavengers using silica gel bonded with perfluoroalkyl chains which separates compounds based on fluorous content.  

Fluorous molecules are selectively retained while non-fluorous compounds are eluted regardless of polarity. This results in a simple two-step separation of fluorous compounds from non-fluorous compounds, giving a purity comparable to traditional chromatography, but much more quickly. Hence, following completion of a reaction using a fluorous-tagged molecule, the reaction mixture is loaded onto a fluorous solid phase. Using a fluorophobic wash, the non-fluorous organic compounds are washed off the material while the fluorous compounds are eluted using a fluorophilic second wash.  

Multiple fraction collection and analysis are not required as there is one organic wash and one fluororous wash. Due to the large separation, loading levels can be very high, and since the separation process is highly reproducible and functional group independent, it can be easily automated.  

The chromatographic properties of sol–gel materials, true chemical sponges that absorb and concentrate molecules at their enormously vast (several hundreds of square metres per gram) inner surface, can be efficiently exploited using fluorinated sol–gels as highly efficient absorbents in a wide variety of environmental decontamination applications ranging from oil-spill cleanup to removing metals and organics from aqueous and vapour media.  

Hence, hydrophobic aerogel ORMOSIL with extremely high surface areas prepared by sol-gel processing of 3,3,3-trifluoropropyl-trimethoxysilane and TMOS (tetramethoxysilane) can separate oil from an oil/water mix, absorbing 4–16 times their own weight of oil; a discovery of fundamental relevance to environmental protection as the impact of oil spills depends on where the oil ends up (right, the Spanish shores near Bilbao are shown after a shipwreck in 1999).  

expensive sol–gel oxides are easily coated on less expensive materials like charcoal or sintered glass beads, fluorinated ORMOSIL are soon likely to find practical use as high-capacity and reusable absorbents for organics and metals in contaminated sites as the sol-gel process versatility allows the chemical sorption properties of the solid material to be tailored to the desired target, such as uranium, chromium, gold or VOCs (volatile organic compounds).  

The potential benefit of this discovery is better understood when one considers that the environmental impact of an oil spill depends on where it ends up, rather than on the absolute amount of oil spilled; and that the greatest impacts occur when oil enters sensitive near-shore habitats such as coral reefs and mangroves whose recovery, once damaged, can take decades.

3.3 Catalysis and polymer synthesis

Fluorous biphasic catalysis, i.e. homogeneous catalytic conversions carried out within a fluorous reaction mixture in which a fluorinated catalyst, organic solvent and reagents share a single phase at the operating temperature and then separate out upon cooling to give easy catalyst separation and recovery, has now been developed as a synthetic tool.  

Applications of fluorinated materials to heterogeneous catalysis, however, are at least as relevant as numerous. As mentioned above, fluorine and fluorne-containing compounds show a strong affinity for CO₂, and heavily fluorinated polymers, being soluble in dense phase carbon dioxide (or “supercritical”, scCO₂), are ideally suited for reactions in this alternative chemical solvent which has recently found practical use in industry for the heterogeneously catalysed synthesis of several fine chemicals.  

Hence, fluorinated dendrimer-encapsulated Pd nanoparticles are active and highly selective for both the reduction of styrene and the carbon–carbon bond forming Heck reaction in scCO₂ (Scheme 2), with facile catalyst recovery. The dark-brown catalyst was easily solubilized in liquid- and scCO₂ (dull-orange solution), with no signs of aggregation or precipitation.
With a similar approach, the aerobic oxidation of alcohols in scCO$_2$ resulted in a significant improvement of the material’s catalytic activity and selectivity compared to the non-fluorinated analogue in the case of either Pt and Pd supported over a fluorinated graphite, and of perruthenate encapsulated in a fluorinated ORMOSIL (sg-TPAP in Scheme 3). The general idea is simple: the catalyst is entrapped in a porous sol–gel fluorinated matrix; the alcohol substrate and O$_2$ dissolve in dense phase carbon dioxide which, upon contact with the powdered hydrophobic sol–gel material, spills the reactants into the pores where the catalyst is entrapped and where the oxidative dehydrogenation takes place, and then it extracts the products.

A thorough choice of the material precursors and sol–gel polycondensation conditions is crucial in affording effective oxidation catalysts as the best activity in a series of increasingly fluorinated ORMOSIL was observed with the fluorinated silica matrix with the low degree of fluorination (10% in molar terms), pointing to a balance between the CO$_2$- and O$_2$-affinity of the matrix and the (relatively polar) alcohol substrate, thus showing how the HLB of a fluorinated sol–gel oxide can be tuned to optimise, for instance, the catalytic activity.

Fluorinated moieties in organic molecules, in fact, are known to segregate from other functional groups (see above in section 2.1), whereas in the growing sol–gel material micelles easily form with the hydrophilic heads pointing towards the strongly hydrogen bonding water/methanol solvent interface and the hydrophobic moiety entrapping the hydrophobic dopant molecules. Therefore, reaction conditions are chosen to minimise such micellization and to prevent burying the reactive dopant molecules in the bulk of the final xerogel.

Further extending a similar approach, fluoruous biphasic catalysis can be conducted in (subcritical) carbon dioxide used to expand a traditional organic solvent and boost solubility thereby replacing the fluoruous liquid with fluorinated silica. In this manner, the fluoruous catalyst is induced to dissolve in the organic solvent by the presence of CO$_2$, and the recovery of the catalyst after the reaction is achieved by simple release of the CO$_2$ pressure (Fig. 4).

Similarly, the immobilization of a perfluoro-tagged palladium catalyst on a fluorinated silica gel affords a recyclable catalyst whose activity in the Suzuki and Sonogashira cross-coupling reactions is comparable to those found in liquid–liquid fluoruous biphasic catalysis (Fig. 5). No fluoruous solvent was needed for the reaction and the isolation and recovery of the catalyst, whereas due to the extreme dispersion of the catalyst absorbed at the ORMOSIL surface, very small amounts of catalysts could be easily handled and the same support can be used for different catalysts, without the need for a separate linker unit.

Stability enhancement upon fluorination can be also exploited to achieve superior performance in heterogeneous catalysis. Hence, fluorinated polyanilines outperform the parent compound polyaniline as the electrode modifier in electrodes consisting of a platinum electrocatalyst covered by a conductive polymer like polyaniline; these are excellent anodes for harvesting electricity in microbial fuel cells.

Similarly to polyaniline, they improve the catalytic activity of the platinum towards the oxidation of hydrogen, a product
of the anaerobic microbial metabolism (Fig. 6). Compared to polyaniline, however, the fluorinated polymers are superior in the protection of platinum from becoming poisoned by metabolic by-products. The high stability of poly(2,3,5,6-tetrafluoroaniline) towards microbial and chemical degradation makes this compound a highly promising candidate for applications in microbially aggressive environments like sewage sludge.

Finally, fluorinated solvents allow the synthesis in supercritical CO₂ of polymer chains with a very narrow molecular weight distribution as well as synthesis of block copolymers using the “controlled” free-radical polymerization techniques known as atom transfer radical polymerization (ATRP), and removing the catalyst in an elegant way.⁵² Hence, for example, using Cu(0), CuCl, a functionalized bipyridine ligand, and an alkyl halide initiator, block copolymers comprised of fluorinated (meth)acrylates and poly(MMA) (MMA = methyl methacrylate) or poly(DMAEMA) (DMAEMA = 2-(dimethylamino)ethyl methacrylate) were recently produced in scCO₂ by ATRP.⁵³

3.4 Sensors and analysis

By exploiting the enhanced O₂ diffusivity across fluorinated substances⁶ and their unique physical and chemical stability, it was discovered recently that the O₂ sensitivity of a hybrid xerogel-based quenchometric sensor composed of n-propyltrimethoxysilane and 3,3,3-trifluoropropyltrimethoxysilane doped with the luminophore tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) ([Ru(dpp)₃]²⁺) is extremely high (Fig. 7).⁵ Such a sensor shows a stable response (constant to within 2%) over a six month period, compared to the five-fold decrease in sensitivity in pure SiO₂-based xerogels and exhibits a sensitivity significantly greater than observed with any previous [Ru(dpp)₃]²⁺-based quenchometric sensor. These findings open the way to the commercial development of second-generation sol–gel oxygen optical sensors that are replacing earliest electrochemical methods to detect this ubiquitous reactant with fast, economic optical detection (Fig. 7, right).⁵⁴

Another advanced application of the increased hydrophobicity of fluorinated interfaces in chemical analysis was recently reported in which detection limits about 50 times more sensitive than any previously obtained by mass spectrometry were achieved.⁵⁵ The technique is based on a soft ionization method in which porous silica surfaces are used to generate gas-phase ions, which are then mass-analyzed. Simple organic modification of the porous silica surface with fluorinated silanes (Fig. 8) largely improves the sensitivity and also enables the surface to absorb analytes from solution selectively, via hydrophobic interactions, allowing extraction (by selective surface absorption) of tiny amounts of analytes from complex matrices containing salts and other contaminants that impede MS analysis without any purification.

Thus, in a series of dilution experiments aimed to demonstrate the sensitivity of the method measuring solution...
concentrations of a peptide commonly used as a sensitivity standard, an impressive lower detection limit of 480 molecules (or 800 yoctomoles: 800 \times 10^{-24} \text{ mol}) was reliably achieved.

4. Economic and environmental aspects

In the 60 years since the serendipitous discovery of PTFE [or poly(tetrafluoroethylene)] in 1938, the chemistry of fluorinated organics has evolved into a well established and articulated research field, and a prosperous industry, in which partly and perfluorinated compounds are prepared either for enhancing the original functionality of the organic compounds (for example, the bioactivity) or for imparting various unique functions originating a cornucopia of applications (Fig. 9).

As might be expected with highly stable and hydrophobic compounds, however, besides the ozone layer depletion action of chlorofluorocarbons, fluorinated materials have a number of environmental and health impacts that have yet to be fully assessed, while global production of fluorochemicals is rising rapidly.

For instance, the surfactant perfluorooctanoic acid (PFOA) used to manufacture PTFE and related waterproof fabrics persists in the environment and causes developmental and other adverse effects in laboratory animals. The compound was found in the blood of people across the world, including those living thousands of miles from the manufacturing sites. Eventually, in June 2005, a report from the US environmental protection agency (EPA) science advisory board concluded the agency should classify the chemical as a “likely” carcinogen in humans.

Therefore, as research on the health, safety and environmental aspects of fluorinated substances is due to provide reliable data soon, production methods should be implemented which are compatible with the environment and with the health of the workers. This means, for instance, that zero-waste production processes should be developed along with a full recycling logic, that in this case is further justified by the high cost of fluorinated organics. Alternatively, the use of fluorinated solvents in fluorous catalytic synthesis can be entirely be prevented by designing catalysts that become soluble in the organic solvent on raising the temperature of the mixture, or, even better, that do not require fluorous solvents at all (Fig. 5).

On the other hand, it may also be noted that fluorine-based surfactants are helping, as solvent boosters, to replace toxic and carcinogenic chlorinated solvents in the dry cleaning industry with supercritical CO$_2$: an economically and environmentally viable technology that is now spreading in the EU after its launch in the US in the mid 1990s.

Clearly, the precautionary sustainability principle here would be to recommend more developments that, like the latter, are beneficial to the economy as well as to the environment. Since fluorine chemistry is a technologically advanced enterprise practiced by leading chemical companies, it might well reveal a field where chemical industry’s new approach to sustainability based on radical productivity increases in resource utilization and production of entirely recyclable products will be implemented at large.

5. Conclusions and future challenges

Fluorinated materials are a vast class of high-performance functional substances having a multitude of applications. Fluorine imparts distinctive properties to fluorinated materials which are increasingly understood (and predicted) in the light of modern developments in quantum chemistry. Furthermore, new materials science and biochemistry methods allow the preparation of sophisticated fluorine-containing materials for targeting advanced applications which are likely to enter ever increasing sectors of modern life. In this sense, the large potential of fluorinated materials remains largely unexplored; the judicious integration of these disciplines will make new strategic applications possible amongst which, biotechnological syntheses and catalytic conversions are only few of the possible novel developments.

In the early 1990s researchers at a petrochemical company were trying to develop a three-way oxidation catalyst to...
selectively convert methane to methanol, with the idea of mimicking the behaviour of the methane monooxygenase enzyme discovered in the early 1980s. The eventual outcome was fluorous phase catalysis as the development of such catalyst was found to be “exceedingly difficult”. The problem of converting natural gas into a valuable oxygenates, however, remains the central problem of heterogeneous catalysis in the petrochemical industry and, therefore, for the global society which continues to burn methane for heat and electricity and so represents a major form of waste.

Similarly, membranes made of the fluorinated polymer Nafion (a perfluorinated polymer that contains small proportions of sulfonic or carboxylic ionic functional groups created by introducing sulfonic acid groups into the bulk polymer matrix of Teflon) has been applied over the past 30 years in fuel cells, thanks to their durability and excellent performance. As the development of new materials for fuel cells is rapidly expanding, novel fluoropolymers will be introduced to meet increasingly demanding requirements as in the case of maintaining stable cell operation for prolonged use at 80 °C (where a heat resistant quasi-solid state electrolyte mainly based on a fluorinated polymer is used).67

New fluorinated materials will play a major role in these and other relevant societal advancements and, as the number of research problems remains open, fluorine chemistry will continue to be a fascinating field of research for many years to come.

Acknowledgements

We started work on fluorinated materials with Prof. Sandro Camperstrini and we thank him for his creative collaboration. Thanks to Prof. David Avnir for many enlightening discussions and to Prof. Frank V. Bright and Rachel M. Bukowski for their openness to collaboration. Our research has been largely funded by the educational activities of the Quality College del CNR, the management educational school whose foundation at Palermo’s CNR owes much to the late Professor Giulio Deganello, to whom this work is dedicated with affection.

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liberates water molecules to the bulk solvent (entropically favoured) while concomitantly, enthalpically favorable dipolar interactions of the C-F bonds with cationic or dipolar residues in the receptor site are retained.


26 Thus, molecular dynamics simulations on mixtures involving water, hydrocarbons, and a variety of fluorinated molecules are currently carried out with the purpose of understanding the nature of the fluorous phase and to establish what kind of intermolecular forces can explain the formation of different phases at the University of Wisconsin at Madison by Professor Sandro Sandore M’s research group. S. Mecozzi, personal communication (March 2003).


34 Hydrolytically stable fluorinates are indeed easily synthesized and commercially available in an ample variety. Along with Fluorochrom, Apollo, FTI chemicals manufacturer ABCR commercializes a variety of such fluorinated metal alkoxides. See: http://www.abcr.de/.


36 G. R. Atkins and R. B. Charters, Fluorochem, Apollo, FTI chemicals manufacturer ABCR commercially available in an ample variety. Along with Fluorochrom, Apollo, FTI chemicals manufacturer ABCR commercializes a variety of such fluorinated metal alkoxides. See: http://www.abcr.de/.


40 “Inverse opal” silica films are obtained adding polystyrene spheres several hundred micrometres in diameter to the silica alkoxide and surfactant precursor sol at the onset of the sol-gel polycellulose. The mixture self-assembles into a regular hexagonal array with the smaller silica particles filling in the gaps between the closely packed polystyrene spheres, in: Z.-Z. Gu, H. Uetsuka, K. Takahashi, R. Nakajima, H. Onishi, A. Fujishima and O. Sato, Angew. Chem. Int. Ed., 2003, 42, 894.


45 For instance, a new easy-to-use hand-held optical sol-gel oxygen sensor (named FOXY-LITE, see: http://www.oceanoptics.com) with a response time of less than 1 s has been commercialized at $1,999 since March 2004 by the US company Ocean Optics Ltd. The sensor uses a fluorescent ruthenium complex immobilized in a silica sol-gel matrix at the probe’s tip. Fluorination of the sol-gel matrix described in ref. 9, however, enhances both sensitivity and stability of the sensor and is likely to be adopted soon by the company.


47 Most big chemical companies produce increasing amounts of fluorinated polymers as high value-added chemicals. For instance, former Italian company Ausimont (now owned by Solvay), in the year 2000 had a revenue of 490 million euros and almost 100 million euros of net tax profit selling fluorinated organics produced in eight plants (three in Italy, one in Germany and four in the US).


50 K. Kannan, S. Corsolini, J. Falandysz, G. Fillmann, K. Senthil Kumar, B. G. Loganathan, M. Ali Mohd, J. Olivero, N. Quwouwe, J. H. Yung and K. M. Aldous, Environ. Sci. Technol., 2004, 38, 4489. DuPont recently agreed pay more than $100 million to help local utilities remove perfluoroctanoic acid (PFOA) from drinking water and fund a study on whether there is a connection between exposure to the chemical and disease in humans as residents near a company’s plant in Virginia who were harmed from drinking water that was contaminated with PFOA released by the facility. C. Hogue, Chem. Eng. News., 2004, 82, 35, 17.

51 It has recently been shown that the real origin of fluorinated carboxylic acids is not PFOA but, more likely, polyfluorinated alcohols that convert to PFOA or other carboxylic acids in the environment: (a) D. A. Ellis, J. W. Martin, A. O. De Silva, S. A. Mabury, M. D. Hurley, M. P. Sulbaek Andersen and T. J. Wallington, Environ. Sci. Technol., 2004, 38, 3316. For an interesting account on the environmental effects of fluorinated organics, see: (b) R. Renner, Environ. Sci. Technol., 2001, 37, 154A.


53 In 2002 ICI and Linde launched a new fluorinated carbon dioxide-based fluid, called Washpoint, to boost solubility in liquid CO2 and replace perchloroethylene as solvent in the dry-cleaning market. The novel technology follows the first commercial dry-cleaning process in liquid CO2 marketed in the US since 1995 by Micell Technologies in partnership with the Hangers chain of dry cleaners (with stores using the technology in the US, Canada and two EU member States as of March 2005).

54 This refers to a new management approach to the environmental issues started in the mid 1980s with environmental certification issues. The British fine chemicals manufacturer Thomas Swan & Co. Ltd. produces a host of fine chemicals with striking selectivity (and purity) in the first multipurpose plant for heterogeneously catalyzed productions in the world. See: http://www.thomas-swann.co.uk.


60 Most big chemical companies produce increasing amounts of fluorinated polymers as high value-added chemicals. For instance, former Italian company Ausimont (now owned by Solvay), in the year 2000 had a revenue of 490 million euros and almost 100 million euros of net tax profit selling fluorinated organics produced in eight plants (three in Italy, one in Germany and four in the US).